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Observation and Assignment of Intermolecular van der Waals Vibrations

Andersen, Jonas; Heimdal, J.; Wallin Mahler Andersen, Denise; Nelander, B.; Larsen, René Wugt

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The Weakly Bound 1:1 Complex of CO_2 and H_2O: Observation and Assignment of Intermolecular van der Waals Vibrations

J. Andersen[a], J. Heimdal[b], B. Nelander[b], D.W. Mahler[a] and R. Wugt Larsen[a]

[a]*Technical University of Denmark, Department of Chemistry, DK–2800 Kongens Lyngby, Denmark*

[b]*Lund University, MAX-IV Laboratory, SE–22100 Lund, Sweden*

The intermolecular interaction between CO_2 and H_2O plays a major role for a multifaceted variety of phenomena in physics, chemistry and biology including the radiation transfer through the Earth's and planetary atmospheres, the early stage of carbonic acid formation and the transport of dissolved CO_2 in the tissues of biological organisms.

The prototypical binary mixed 1:1 complex formed between CO_2 and H_2O has accordingly been investigated intensively by both theory and experiment. A recent comprehensive work reporting a complete high-level 5-D *ab initio* intermolecular potential energy surface composed of 23 000 single-point energies indicates that the global potential energy minimum has a planar and T-shaped geometry of C_{2v} symmetry with the oxygen atom of H_2O bound to the C atom and the H atoms pointing away from the CO_2 molecule as shown in Fig. 1.[1]

The weakly bound nature of the CO_2–H_2O system results in rather small perturbations of the intramolecular vibrational transitions relative to the vibrational transitions of the isolated subunits. The total shift of the zero-point energy contribution to D_0 caused by perturbations of intramolecular vibrational transitions is in the order of 5 cm^{-1}. A reliable determination of the system's zero-point energy thus relies completely on accurate band origins for the set of five intermolecular vibrational transitions introduced by the van der Waals interactions.[1]

Terahertz absorption spectra have recently been obtained at the infrared beam-line for CO_2/H_2O mixtures embedded in cryogenic neon matrices at 2.8 K. Several millimeter thick matrices of neon doped with CO_2 and H_2O were deposited at 3.6 K on a gold-plated OFHC copper mirror inside an immersion helium cryostat (IHC-3) modified for matrix isolation spectroscopy.[2] Single-beam spectra were collected by the Bruker IFS 120 FTIR spectrometer located at the beam-line.

Based upon relative concentration dependency measurements, heavy isotope substitutions and complementary mid-infrared studies of perturbed intramolecular vibrational transitions, two high-frequency intermolecular vibrational transitions have been observed for the H_2O–CO_2 van der Waals complex at 101.8 and 166.2 cm^{-1} as shown in Figure 2. These large-amplitude

intermolecular modes have been assigned to out-of-plane wagging and in-plane rocking of the H_2O subunit, respectively, and provide crucial observables for benchmark theoretical descriptions of this van der Waals system's flat intermolecular potential energy surface.

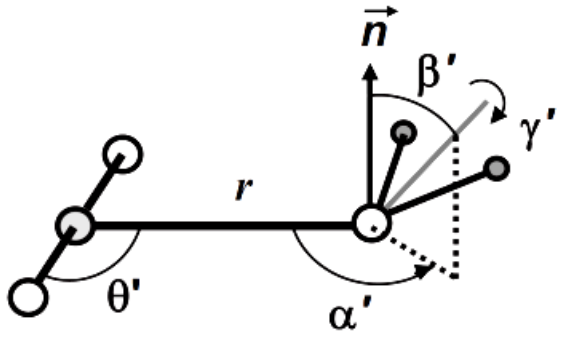

Figure 1: The five intermolecular coordinates (r, θ', α', β', γ') specifying the configuration of the weakly bound H_2O–CO_2 van der Waals complex. The white circles represent oxygen atoms and the grey circles carbon and hydrogen.

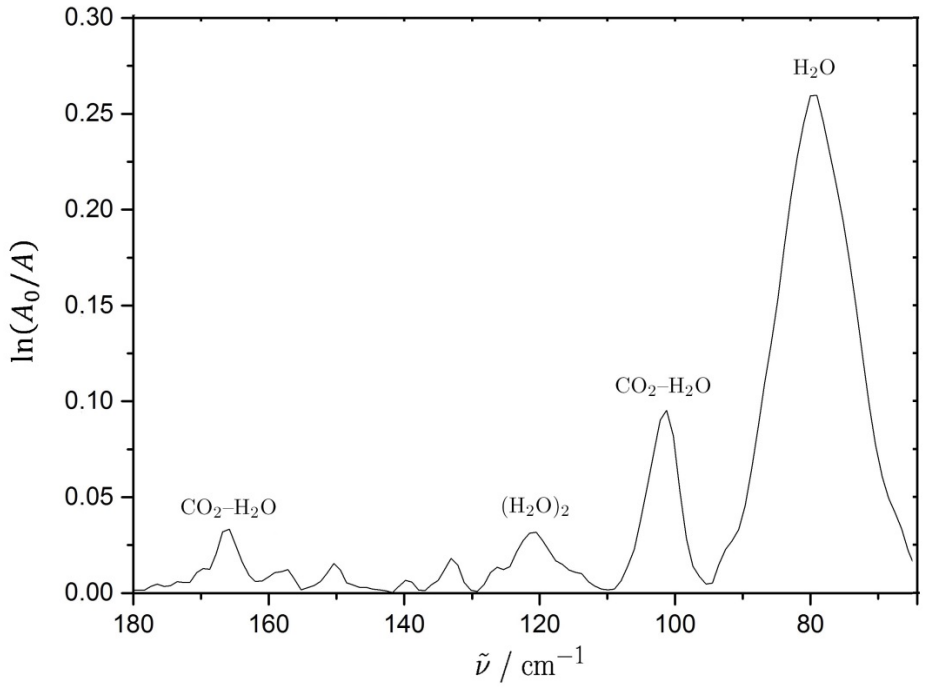

Figure 2: The assigned transitions for the recorded THz spectra of CO_2/H_2O mixtures embedded in solid neon matrices at 2.8 K.

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